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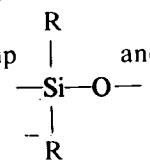
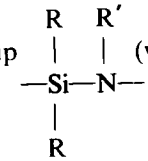
Brief 66-10194

NASA TECH BRIEF

Silazane Polymers Show Promise for High-Temperature Application

The problem:

To develop polymers that will be useful as adhesives, structural plastics, elastomers, and laminating resins in extreme environments. Certain chemical (isoelectronic and isosteric) similarities between the silicone group  and the silazane group  (where R and R′ are organic radicals) have suggested that with the proper substituents on the silicon and nitrogen atoms, it should be possible to develop silazane polymers having a useful temperature range beyond that of the silicones.

The solution:

A number of intermediate compounds and polymers containing silicon–nitrogen bonds and showing promise as high temperature coatings and elastomers that exhibit stability to temperatures in the range of 300° to 400° C.

How it's done:

Several silazane polymers were prepared by reacting dimethyldichlorosilane [$(CH_3)_2SiCl_2$] with various organic diamines [$R(NH_2)_2$]. The diamines used included ethylenediamine; 1,3-propanediamine; 1,6 hexanediamine; 1,4-phenylenediamine; piperazine; benzidine; and 4,4′-methylenedianiline.

A one-step reaction involving a 1:1:2 molar ratio of dimethyldichlorosilane, ethylenediamine, and triethylamine as an acid acceptor produced a polyethylenediaminesilazane. The reaction was conducted in a one liter, three-neck flask equipped with a stirrer, dropping funnel, and reflux condenser. To this flask was added a solution of 0.2 mol of dimethyldichlorosilane in 200 ml of dry benzene. A separate solution containing 0.2 mol of ethylenediamine and 0.4 mol of triethylamine in 100 ml of dry benzene was then added dropwise, with constant stirring, over a 90-minute period. The resulting solution was then refluxed for 3.5 hours. At the end of this time, the triethylamine hydrochloride produced in the reaction was filtered off, and the benzene was evaporated under reduced pressure. The product, containing approximately 67% solids, was applied to an aluminum plate; the excess solvent was removed by heating at 70° C for 18 hours, and the resulting film was cured at 204° C for 2 hours and then at 315° C for 1 hour. The transparent, smooth, elastomeric film could be peeled from the plate, but had relatively low strength. It remained unchanged in physical appearance and retained its elasticity after standing for 17 months under normal atmospheric conditions.

The silazanes prepared by reacting dimethyldichlorosilane with the other diamines yielded foamed elastomers, rigid foamed solids, powders, waxes, and viscous liquids of varying properties.

An analogous series of polymers, prepared by reacting diphenyldichlorosilane [$(C_6H_5)_2SiCl_2$] with four different organic diamines, in the manner described above, yielded polymers ranging from tacky gels to brittle solids. When cured at 400° C, some of these materials formed stable polymers.

Several potentially useful polymers were prepared by chain-opening reactions between equimolar amounts of hexaphenylcyclotrisilazane and various

(continued overleaf)

diols. Some of these materials exhibited good film and fiber forming properties. One of these materials is stable at temperatures up to 500° C.

Notes:

1. These materials must still be classed as developmental and several are under evaluation.
2. Further information concerning these materials is given in "New Polymers for High Temperature Applications" by Robert E. Burks of Southern Research Institute and James D. Byrd and James E. Curry of Marshall Space Flight Center, in NASA SP-5030, Symposium on Technology Status and Trends, April 21-23, 1965, available from Clearinghouse for Federal Scientific and Technical Information, Springfield, Virginia, 22151. Inquiries may also be directed to:

   Technology Utilization Officer
   Marshall Space Flight Center
   Huntsville, Alabama, 35812
   Reference: B66-10194

Patent status:

Inquiries about obtaining rights for the commercial use of this invention may be made to NASA, Code GP, Washington, D.C., 20546.

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